reduction of the cyanide derivative of cytochrome *c* oxidase is easily understood in terms of exciton resonance interactions.[11] Should the hemes be juxtaposed a maximal heme–heme distance of 9 A can be calculated. An important reservation must be retained and that is that no aggregation studies have been carried out on heme a systems. Work directed toward that goal is presently under way.

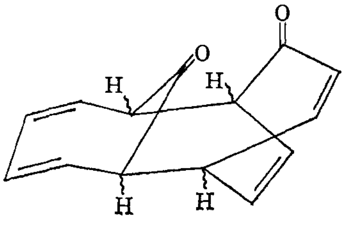
Acknowledgments. The authors wish to thank M. Mednieks for preparing the heme octapeptide, R. Purvinas and A. Ruiter for technical assistance, and Professor G. Guidotti for helpful discussions.

Communications to the Editor

Stereochemistry and Mechanism of a Tropone Photodimerization

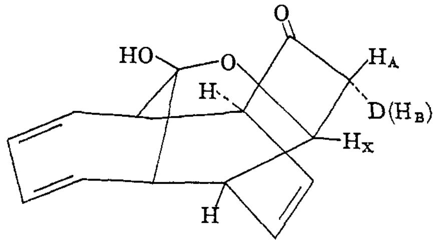
Sir:

We have recently described the formation of a tricyclo[6.3.2.1^{2,7}]tetradeca-3,5,9,12-tetraene-11,14-dione (I) of unspecified stereochemistry as a major product of tropone photodimerization in acetonitrile.[1] This reaction formally represents a (6 + 4) π electron cycloaddition, a process not normally favored for concerted photochemical *cis* addition[2] between two polyene systems.[3] We now report observations which permit assignment of stereochemistry in this series and offer data bearing on the mechanism of the photodimerization process leading to I.



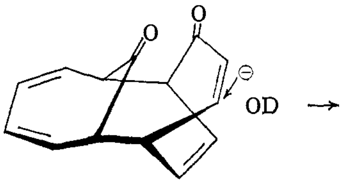
I

Brief treatment of photodimer I with cold dilute NaOD produces two crystalline *hydration products*, mp 201 and 187° dec. The 201° product (ν^{KBr} 3400, 1717 cm^{-1}) retains the diene portion of precursor I but lacks the unsaturated ketone chromophore; it contains one carbon-bound deuterium[4] and one hydroxyl group (by nmr exchange). The nmr of an undeuterated sample shows an ABX pattern with $\delta_A = 2.60$, $\delta_B = 2.87$, $\delta_X = 4.75$; $|J_{AB}| = 17$ Hz, $|J_{AX}| = 5$ Hz, $|J_{BX}| = 1$ Hz.[5] In the deuterated material the B proton signal is absent, and the X proton is a double doublet indicating further coupling of X to a single vicinal proton with $|J| = 7$ Hz. The spectroscopic data agree with the hemiketal structure II which, moreover, rationalizes the observed resistance of the compound to oxidation by chromium trioxide in pyridine.

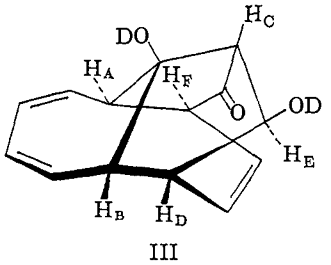


II

The 187° hydration product contains *no carbon-bound deuterium;* it shows ultraviolet absorption similar to II, a single carbonyl maximum at 1748 cm^{-1}, and two hydroxyl groups (nmr). These facts suggest a mechanism wherein attack of deuterioxide on the enone double bond leads to an enolate anion which undergoes internal aldolization to the β-hydroxy ketone III faster than it suffers external deuteron uptake on carbon.



I



III

The 100-MHz nmr spectrum (Figure 1)[6] of the 187°

---

(1) A. S. Kende, *J. Am. Chem. Soc.*, 88, 5026 (1966).

(2) As originally formulated, the Hoffmann–Woodward rules[3] for concerted cycloadditions apply to *cis* additions; for *trans* cycloadditions, which may be observed in sufficiently flexible systems, a reversal of the usual rules is predicted. We are indebted to Professor R. Hoffmann for calling our attention to this point.

(3) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965).

(4) Mass spectrometric analyses were carried out by the Morgan-Shaffer Corp., Montreal, Canada. All new compounds gave satisfactory combustion analyses and exhibited mass spectrometric fragmentation patterns in accord with the postulated structures. We are grateful to L. Brancone and W. Fulmor for the analytical and spectrophotometric data and to Dr. J. Karliner for interpretation of the mass spectra.

(5) These values were determined at 60 MHz in CDCl$_3$ solution; the δ values refer to parts per million downfield relative to internal tetramethylsilane.

(6) We are grateful to Dr. L. A. Wilson (Rutgers University) for the data of Figure 1, which were measured for a pyridine-d_5 solution (after exchange of active hydrogen) using a Varian HA-100 spectrometer.

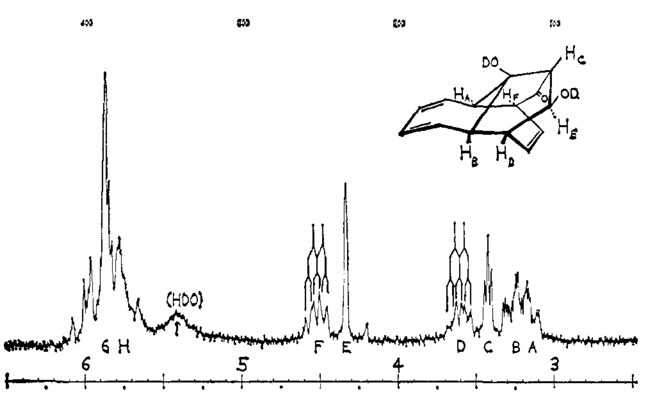
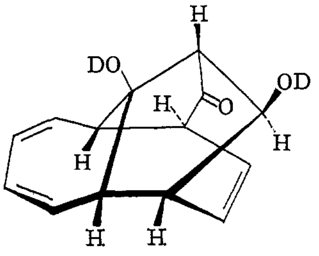
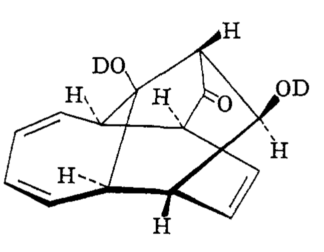
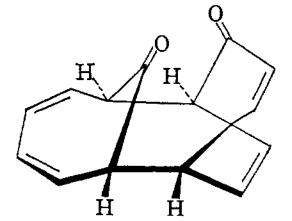


Figure 1. Nmr spectrum at 100 MHz of compound III in pyridine-d_5; scale is in parts per million downfield from internal tetramethylsilane.

hydration product confirms structure III. Spin decoupling demonstrates the homoallylic coupling $|J_{DF}| = 3.4$ Hz[7] and the vicinal couplings $|J_{AF}| = 5.6$ Hz and $|J_{BD}| = 5.4$ Hz.[8] The vicinal couplings require the stereochemistry of the ABDF region to be as depicted in structure III. Such alternatives as IV or V are nearly strain free but should exhibit dissimilar values for J_{AF} *vs.* J_{BD}. Because epimerization of protons A, B, D, or F could not have occurred during formation of III, the stereochemistry of photodimer I must parallel that of III, as shown in formula VI.[9]


IV


V


VI

Since proton C is not coupled to the olefinic region or to proton F, the narrow C triplet must arise from long-range coupling of the W type[10] to both protons A and B, with $|J_{AC}| = |J_{BC}| = 1.8$ Hz. The identity of proton C is confirmed by the following evidence. The prolonged action of deuterated base upon the 201° hydration product II or the 187° product III produces a *C-monodeuterated* compound $C_{14}H_{13}DO_3$ which exhibits an nmr spectrum identical with that of III except for the absence of the signal for C near δ 3.4. Control experiments establish that this compound is simply III-d_1; thus, kinetically controlled hydration of photodimer I gives predominantly II whereas the thermodynamic product is the tetracyclic ketone III, and the observed isotopic exchange of proton C probably occurs through a retroaldol equilibrium. The stereochemistry of the secondary hydroxyl group in III is provisionally assigned as depicted since vicinal couplings CE or ED are not observed.

Reaction Multiplicity. Stereochemistry VI requires photoaddition of the first tropone molecule to the second in a *cis* manner. The question then arises whether this (6 + 4) π cycloaddition is a concerted or stepwise process. It can be shown that with light above 300 mμ the rate of tropone disappearance (0.04 *M*) is unaffected by the presence of 0.1 *M* naphthalene (E_T = 61 kcal). However, the use of ferrocene as quencher at 0.02 *M* concentration completely arrests the photodimerization process. Anthracene (E_T = 41 kcal) at this concentration also quenches the disappearance of tropone and further serves to implicate a triplet intermediate in the reaction. Moreover, fluorenone (E_T = 53 kcal) efficiently sensitizes the photodimerization of tropone. Under conditions such that fluorenone absorbs 70–80% of incident light, the disappearance of tropone has a relative quantum yield approximately 85% of that for the direct irradiation, and the sensitized reaction produces the three known photodimers[1] in the same ratio as observed in the direct reaction. Since no change in the relative proportions of the three dimers occurs during direct photodimerization, no one dimer is a precursor of another. All of these observations implicate a triplet of energy between 41 and 53 kcal as the principal intermediate leading not only to the major dimer VI but also to the other two dimers present in the mixture. Since the excited reactive species has triplet multiplicity, the *concerted* formation of both new σ bonds in the generation of VI is improbable, and the apparent formal violation of the Hoffmann–Woodward rules is accommodated by a *stepwise* process. Tropone thus joins cyclopentenone[11] and cyclohexenone[12] among the unsaturated ketones which undergo photodimerization by triplet intermediates.

---

[7] Compare, for example, the 3.5-Hz homoallylic coupling in eleutherin reported by D. W. Cameron, G. I. Kingston, N. Sheppard, and Lord Todd, *J. Chem. Soc.*, 98 (1964).

[8] The respective assignments of vicinal pairs AF and BD in terms of formula III are arbitrary since present data do not allow reliable distinction between the two possibilities. The reversed assignment would not invalidate our stereochemical argument.

[9] Stereochemistry VI has been recently proposed by T. Tezuka, Y. Akasaki, and T. Mukai, *Tetrahedron Letters*, 1397 (1967), on the basis of nmr data on the photodimer which exclude a skeletal stereochemistry corresponding to V. These workers, however, do not appear to have considered the alternative having the stereochemistry corresponding to *trans* derivative IV.

[10] See J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).

[11] P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966); J. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5672 (1966).

[12] E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

Andrew S. Kende
Organic Chemical Research Section, Lederle Laboratories Division
American Cyanamid Company, Pearl River, New York 10965

John E. Lancaster
Research Service Department, Central Research Division
American Cyanamid Company, Stamford, Connecticut 06904

Received June 15, 1967

The Reaction of Amine Anions with *p*-Toluenesulfonyl Azide. A Novel Azide Synthesis

Sir:

Since its initial disclosure in 1953, the elegant procedure of Doering and De Puy[1] for the preparation of